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MATHEMATICAL MODELS FOR COMPARATIVE STUDY OF EXPERIMENTAL AND THEORETICAL REFRACTIVE INDEX OF BINARY LIQUID MIXTURES

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Abstract

This paper presents the nature of interaction between component molecules in the binary liquid mixtures and enables us to identify a suitable mathematical model for predicting the refractive index of various binary liquid mixtures. A comparative study of refractive index of binary liquid mixtures such as 1,4-dioxane - water, Glycerol - Water and Glycerol - Methanol having industrial applications are analyzed at temperature 304K for different concentrations [20,40,60,80 &100%]. In the present study Refractive Index values were determined by experiments and theoretical values obtained by various mathematical models such as Lorentz – Lorenz relation, Gladstone- Dale equation, Weiner's relation, Heller's (H) equation, Arago-Biot equation were compared. The experimental data were utilized to test the capability prediction of Lorentz-lorenz, Weiner, Heller, Gladstone-Dale, Arago-Biot models. Result analysis revealed that the Arago-Biot and Gladstone-Dale model is best suitable for calculating the refractive index in the binary liquid systems of 1,4 dioxane - water whereas Lorentz-lorenz model is the best suitable method for calculating the refractive index of Glycerol- Water and Glycerol-Methanol binary liquid systems.

Key words: *binary liquid mixtures, refractive index, mathematical models, methanol, 1, 4-dioxane, glycerol.*

1. Introduction

The refractive index is one crucial physicochemical property of a material characterizing its ability to bend light and is the most important optical property of liquid state which provides information about molecular interactions present in the liquid State [1-2]. Refractive index measurements in combination with density, boiling point, melting point and other analytical data are very useful industrially. Measuring the refractive index plays a vital role in various scientific, engineering, and industrial applications, including sensing, material characterization, solution analysis, and optical device design [3]. Understanding the refractive index behavior of liquid mixtures is particularly important in fields like chemistry, pharmaceuticals, and food science. The refractive index measurement of binary mixtures is studied for many reasons. It is essential for the determination of composition of binary liquid mixtures. The knowledge of refractive index property at different temperatures of liquid mixtures is an important step for their structure and characterization [1-2]. The general applicability of refractive index in chemical analysis and industry are revealed in literature survey. Many researchers have been studied the theoretical refractive index measurements by the refractive index mixing rules [3].

The chemicals chosen for this study are important in industrial and scientific context because of their applications. 1, 4-dioxane is a solvent with many commercial and industrial uses in synthesis of other chemicals, adhesives, sealants, and polyethylene terephthalate (PET) plastics, it also used as a processing aid, functional fluid, and dry film lubricant, printing inks, a purifying agent in the manufacture of pharmaceuticals, and found as a contaminant in some consumer products, such as soaps, detergents, deodorants, shampoos, and cosmetics [4-6].

Glycerol or glycerin is a versatile compound widely used across industries for its hygroscopic, non-toxic, and water-soluble properties. In pharmaceuticals and cosmetics, it acts as a moisturizer, emollient, and solvent in skincare products, medications, and toothpaste. It is a humectant and preservative in food, enhancing moisture and shelf life. Industrially, glycerol serves in antifreeze, plasticizers, and explosives like nitroglycerin. It is a key ingredient in chemical synthesis, biofuels, and agriculture, used in animal feed and pesticides. Additionally, it finds applications in lubricants, textiles, printing, and de-icing solutions, making it essential across numerous fields [7],

Methanol, a simple alcohol, has diverse applications across industries due to its chemical versatility. It is a key feedstock in the production of formaldehyde, acetic acid, and other chemicals used in plastics, adhesives, and paints. In energy, methanol serves as a fuel or fuel additive, including in biodiesel production and as a hydrogen carrier for fuel cells. It is also used as a solvent in pharmaceuticals, antifreeze in automotive fluids, and a denaturant for ethanol. Additionally, methanol is vital in producing synthetic materials like resins and fibers and plays a role in wastewater treatment for denitrification processes. Its clean-burning properties make it a promising alternative fuel in reducing carbon emissions [8].

This paper investigated the effectiveness of various mathematical models in predicting the refractive index of liquid mixtures compared to experimental measurements. Understanding the relationship between the components of a mixture and its refractive index is essential for various applications. The experimental section will involve the measurement of refractive indices for different compositions of the chosen liquid mixture. This will be achieved using an instrument like Abbes refractometer which allows for precise and reliable determination of refractive index. The theoretical section will explore established models and equations used to predict the refractive index of mixtures based on the properties of their individual components. Various models, like the Lorentz-Lorenz relation, Gladstone-Dale, Weiner, Heller, Newton and Arago-Biot equation, will be employed and compared to the experimental data [9-12].

By comparing the experimental and theoretical results, the project will evaluate the accuracy and limitations of the employed theoretical models in predicting the refractive index of the specific liquid mixture. Furthermore, the investigation may reveal interactions and deviations between the components of the mixture that are not captured by the theoretical models.

This study will contribute to a better understanding of how the refractive index of liquid mixtures behaves and provide valuable information for further research and applications in various fields.

2. Material and Method

The chemicals were purchased from Merck and were of analytical grade of purity greater than 99%. These chemicals were used as provided by the supplier without any further purification. The binary mixtures (50 ml) of 1,4-dioxane-water, Glycerol-water and Glycerol-methanol of desired concentrations 20,40,60,80 &100% were prepared by mixing appropriate volume fractions of liquid-1 & liquid-2 of respective binary liquid mixtures as given in Table-1. Refractive index values are measured using thermostatically controlled Abbe refractometer having accuracy less than 0.0001 units at 25 ^{0}C. Density values were measured using specific gravity method. The mass of the liquid was measured using a K-Roy make electronic balance, with an accuracy of ±0.0001gm.

Table 1: composition of binary liquid mixtures

Serial No.	% composition	Volume of Liquid-1 (ml)	Volume of Liquid-2 (ml)	Total volume (ml)
1	0%	0 ml	50 ml	50 ml
2	20%	10 ml	40 ml	50 ml
3	40%	20 ml	30 ml	50 ml
4	60%	30 ml	20 ml	50 ml
5	80%	40 ml	10 ml	50 ml
6	100%	50 ml	0 ml	50 ml

3. Mixing Rules

Following mixing rules were used for the calculation of refractive index of all three binary liquid mixtures under investigation.

3.1 Arago-Biot (AB) Equation:

Arago-Biot (A-B), assuming volume additively, proposed the following relation for refractive index of binary liquid mixtures

$$n_m = \varphi_1 * n_1 + \varphi_2 * n_2 \qquad (1)$$

Where, $Ø_1 = W_1/ þ_1$ = Volume fraction of the pure component 1

$Ø_2 = W_2/ þ_2$ = Volume fraction of the pure component 2

W_1= Weight Fractions of the Pure Component 1

W_2= Weight Fractions of the Pure Component 2

$þ_1$ = Density of the Pure Component 1

$þ_2$ = Density of the Pure Component 2

n_m= Refractive index of mixture

n_1= Refractive index of the pure component 1

n_2= Refractive index of the pure component 2

3.2 Gladstone-Dale relation (G-D):

The Gladstone-Dale relation is used for optical analysis (determination of compositions from optical measurements), or to calculate the density of a liquid for use in fluid dynamics. The relation has also been used to calculate the refractive index. Gladstone-Dale (G-D) equation for predicting the refractive index of binary liquid mixture is as follows:

$$(n_m - 1) = \varphi_1(n_1 - 1) + \varphi_2(n_2 - 1) \qquad (2)$$

Where,

n_m= Refractive index of the mixture

n_1= Refractive index of the Pure component 1

n_2= Refractive index of the Pure component 2

$Ø_1$= Volume fraction of the pure component 1

$Ø_2$= Volume fraction of the Pure component 2

3.3 Newton Equation (N):

Newton (N) gave the following equation

$$(n_m^2 - 1) = \varphi_1(n_1^2 - 1) + \varphi_2(n_2^2 - 1) \quad (3)$$

Where,

$Ø_1 = W_1/ þ_1$ = Volume fraction of the pure component 1

$Ø_2 = W_2/ þ_2$ = Volume fraction of the pure component 2

W_1= Weight Fractions of the Pure Component 1

W_2= Weight Fractions of the Pure Component 2

$þ_1$ = Density of the Pure Component 1

$þ_2$ = Density of the Pure Component 2

n_m= Refractive index of mixture

n_1= Refractive index of the pure component 1

n_2= Refractive index of the pure component 2

3.4 Heller's Equation (H):

Heller's (H) equation is given by

$$\left[\frac{n_m - n_1}{n_1}\right] = \frac{3}{2} * \left[\frac{m^2 - 1}{m^2 + 2}\right]\varphi_2 \quad (4)$$

Where,

$m = n_2/n_1$

$Ø_2 = W_2/ þ_2$ = Volume fraction of the pure component 2

W_2= Weight Fractions of the Pure Component 2

$þ_2$ = Density of the Pure Component 2

n_m= Refractive index of mixture

n_1= Refractive index of the pure component 1

n_2= Refractive index of the pure component 2

3.5 Weiner's relation (W):

Weiner's (W) relation may be represented as

$$\left[\frac{n_m^2 - n_1^2}{n_m^2 + 2n_1^2}\right] = \left[\frac{n_2^2 - n_1^2}{n_2^2 + 2n_1^2}\right] * \varphi_2 \qquad (5)$$

Where,

$Ø_2$ = W_2/ $þ_2$ = Volume fraction of the pure component 2

W_2= Weight Fractions of the Pure Component 2

$þ_2$ = Density of the Pure Component 2

n_m= Refractive index of mixture

n_1= Refractive index of the pure component 1

n_2= Refractive index of the pure component 2

3.6 Lorentz-Lorentz (L-L):

Lorentz-Lorenz (L-L) relation for refractive index is based on the change in the molecular interaction with volume fraction:

$$\left[\frac{n_m^2 - 1}{n_m^2 + 2}\right] * \left(\frac{1}{\rho_m}\right) = \varphi_1 \left[\frac{n_1^2 - 1}{n_1^2 + 2}\right] + \varphi_2 \left[\frac{n_2^2 - 1}{n_2^2 + 2}\right] \qquad (6)$$

Where, $Ø_1$ = W_1/ $þ_1$ = Volume fraction of the pure component 1

$Ø_2$ = W_2/ $þ_2$ = Volume fraction of the pure component 2

W_1= Weight Fractions of the Pure Component 1

W_2= Weight Fractions of the Pure Component 2

$þ_1$ = Density of the Pure Component 1

$þ_2$ = Density of the Pure Component 2

n_m= Refractive index of mixture

n_1= Refractive index of the pure component 1

n_2= Refractive index of the pure component 2

The values of Average percentage error (APE) in experimental values and theoretically calculated refractive indices values from various mixing rules [4] were calculated by using the following equation,

$$APE = \frac{1}{n} * \left[\frac{Sum(R.I.exp - R.I.cal)}{R.I.exp} \right] * 100 \quad (7)$$

4. Result and Discussion

In the present study, refractive index was determined for binary mixtures of 1, 4-dioxane - water, Glycerol-water and Glycerol-methanol of different compositions (20, 40, 60, 80 & 100%) at a temperature 304K. The experimental values of density and refractive index data, obtained at 304K are reported in Table 2, 3 & 4 respectively.

Table 2: Density and refractive index data, obtained at 304K for System-I: 1, 4-dioxane - water

% Composition 1,4 –dioxane	Volume fraction of 1,4 -dioxane ($Ø_1$)	Volume fraction of water ($Ø_2$)	Weight of mixture (W) g	Density (þ) g/cm^3	Refractive index (n)
0 % (Pure water)	0	1	10.7230	0.995	**1.3300**
20%	0.2	0.8	10.9165	1.0123	**1.3455**
40%	0.4	0.6	11.1562	1.0345	**1.3634**
60%	0.6	0.4	11.2864	1.0472	**1.3782**
80%	0.8	0.2	11.3726	1.0552	**1.3963**
100 % (Pure 1,4 dioxane)	1	0	11.1002	1.0299	**1.4144**

Table 3: Density and refractive index data, obtained at 304K for system II: glycerol - water

% Composition glycerol	Volume fraction of Glycerol ($Ø_1$)	Volume fraction of Water ($Ø_2$)	Weight of mixture (W) g	Density (þ) g/cm^3	Refractive index (n)
0 % (Pure water)	0	1	10.899	0.995	**1.33**
20%	0.2	0.8	11.321	1.0335	**1.3702**
40%	0.4	0.6	12.115	1.1060	**1.3863**
60%	0.6	0.4	12.734	1.1625	**1.4114**
80%	0.8	0.2	13.328	1.2167	**1.4426**
100% (Pure glycerol)	1	0	13.727	1.2531	**1.4626**

Table 4: Density and refractive index data, obtained at 304K for system III: glycerol - methanol

% Composition of glycerol	Volume fraction of glycerol (Ø1)	Volume fraction of methanol (Ø2)	Weight of mixture (W) g	Density (þ) g/cm^3	Refractive index (n)
0% (Pure methanol)	0	1	8.6182	0.7910	**1.3405**
20%	0.2	0.8	10.1875	0.9350	**1.3742**
40%	0.4	0.6	11.4700	1.0527	**1.4034**
60%	0.6	0.4	12.3650	1.1349	**1.4285**
80%	0.8	0.2	12.8925	1.1832	**1.4426**
100% (Pure glycerol)	1	0	13.7271	1.2599	**1.4646**

Using above mentioned six mixing rules namely Arago-Biot (A-B) , Gladstone – Dale (G-D), Newton(N), Heller(H), Weiner's(W) and Lorentz-Lorentz (L-L) relations the refractive index for all the binary liquid mixtures has been evaluated and are reported in **Table 5,6 & 7 respectively**.

Table 5: Refractive index data from the calculation by using the mathematical models: system I: 1, 4-dioxane-water

% composition of 1,4 dioxane	Experimental R.I.	A-B	G-D	N	H	W	L-L
0 % (Pure water)	1.3330	1.3300	1.3300	1.3300	1.3289	1.3299	1.3299
20%	1.3455	1.3468	1.3468	1.3473	1.3489	1.3465	1.3503
40%	1.3634	1.3634	1.3634	1.3714	1.3754	1.3634	1.3772
60%	1.3782	1.3782	1.3782	1.3871	1.3865	1.3903	1.4003
80%	1.3963	1.3963	1.3963	1.4042	1.4162	1.3971	1.4221
100 % (Pure 1,4 dioxane)	1.4144	1.4144	1.4144	1.4144	1.4144	1.4144	1.4286

Table 6: **Refractive index data from the calculation by using the mathematical models: system II: glycerol- water**

% composition of glycerol	Experimental R.I.	A-B	G-D	N	H	W	L-L
0 % (Pure water)	1.3330	1.3300	1.3300	1.3300	1.3282	1.3299	1.3299
20%	1.3702	1.3565	1.3565	1.3575	1.3551	1.3563	1.3702
40%	1.3863	1.3830	1.3830	1.3845	1.3820	1.3821	1.3863
60%	1.4114	1.4096	1.4096	1.4111	1.4089	1.4092	1.4114
80%	1.4426	1.4361	1.4361	1.4371	1.4357	1.4358	1.4426
100% (Pure glycerol)	1.4626	1.4626	1.4626	1.4626	1.4626	1.4626	1.4626

Table 7: **Refractive index data from the calculation by using the mathematical models: system III: glycerol- methanol**

% composition of glycerol	Experimental R.I.	A-B	G-D	N	H	W	L-L
0% (Pure methanol)	1.3405	1.3405	1.3405	1.3405	1.3389	1.3404	1.3404
20%	1.3742	1.3653	1.3653	1.3693	1.3641	1.3651	1.3742
40%	1.4034	1.3901	1.3901	1.3965	1.3892	1.3898	1.4034
60%	1.4285	1.4150	1.4150	1.4196	1.4143	1.4146	1.4285
80%	1.4426	1.4398	1.4398	1.4399	1.4395	1.4396	1.4425
100% (Pure glycerol)	1.4646	1.4646	1.4646	1.4695	1.4646	1.4646	1.4646

The experimental values of refractive index are compared with the predicted results from the above-mentioned mixing rules and the average percentage errors were determined and are given in **Table 8, 9 & 10 respectively**. The plot of Average percentage error (APE) against the percentage composition for different binary liquid mixtures are shown in **Fig 1, 2 & 3**

Table 8: APE for system I: 1,4 dioxane - water

% composition of 1,4 dioxane	% error A-B	% error G-D	% error N	% error H	% error W	% error L-L
pure water	0	0	0	0.07594	0.000752	0.007519
20	-0.09765306	-0.09765	-0.12914	-0.24748	-0.06986	-0.35449
40	-0.0285568	-0.02186	-0.16934	-0.88009	0.005867	-1.00844
60	-0.02185568	-0.02185568	-0.21853	-0.59639	-0.87717	-1.60126
80	-0.08636679	-0.08636679	-0.16478	-0.63307	-0.05801	-1.84765
pure 1,4 dioxane	0	0	0	0	0	-1.00179

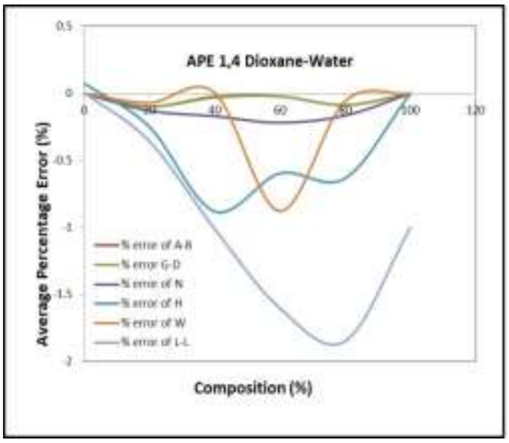

Fig.1: composition of 1,4 dioxane Vs APE (1,4 dioxane-water system)

Table 9: APE for system II: glycerol- water

% composition of glycerol	% error A-B	% error G-D	% error N	% error H	% error W	% error L-L
Pure water	0	0	0	0.131018	0.003008	0.000752
20	0.999394262	0.999394	0.923657	1.101131	1.016618	0.00073
40	0.234289342	0.234289	0.124175	0.309707	0.301518	0.000721
60	0.130504092	0.130504	0.024384	0.179887	0.157994	0.001417
80	0.447825302	0.447525	0.379572	0.471684	0.465826	-0.00069
pure glycerol	0	0	0	0	0	0.001367

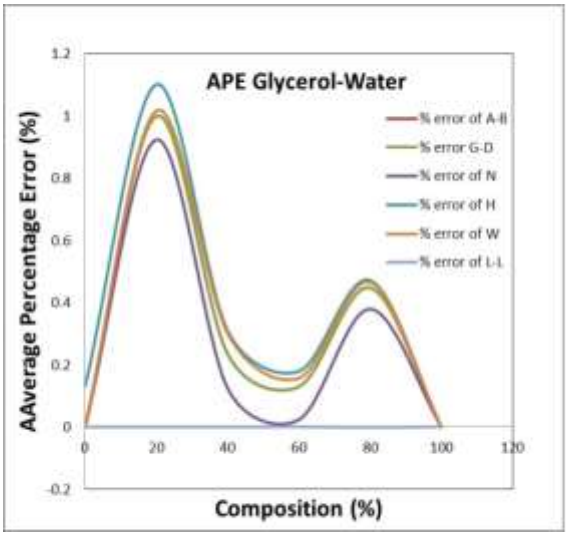

Fig.2: composition of glycerol Vs APE (glycerol-water system)

Table 10: APE for system 3: Glycerol -Methanol

% composition of glycerol	% error A-B	% error G-D	% error N	% error H	% error W	% error L-L
pure methanol	0	0	0	0.114983	0.000746	0.000746
20	0.648499181	0.648499	0.357650	0.738226	0.664362	0.000146
40	0.943694689	0.943695	0.491514	1.009591	0.968349	0.000713
60	0.946840830	0.946841	0.624344	0.989999	0.971621	0.000700
80	0.190489394	0.190489	0.183557	0.211858	0.207958	0.000139
pure glycerol	0	0	-0.3340000	0	0	0.000546

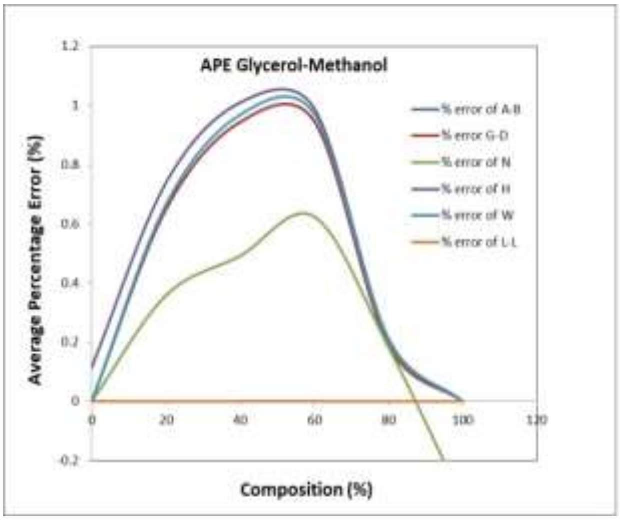

Fig.3: % composition of glycerol Vs APE (glycerol-methanol system)

The refractive index values were calculated from six theoretical mixing rules shows the excellent agreement with the experimental values. The deviation of experimental refractive index from theoretical refractive index value was calculated in terms of average percentage error (APE) for the system under investigation.

From the Above graphs we can conclude that the A-B and G-D models are best suited for calculating the refractive index of 1, 4-dioxane - Water binary liquid mixture and L-L model is best suited for calculating the refractive index of binary system, Glycerol-water and Glycerol - Methanol both. For 1, 4-dioxane - Water binary liquid mixture, all the mixing rules shows negative APE whereas for other two systems, mixing rules shows the positive deviations. At 50 % composition (0.5 volume fraction) APE is the lowest than at other compositions in case of Glycerol-water system whereas APE is the highest than at other compositions in case of Glycerol-Methanol system. However in case of 1, 4-dioxane - Water binary liquid mixture, mixed behavior is observed. The deviation between the theoretical and observed values of refractive index for all the systems can be reduced by taking excess volume in to consideration [13], which is an indirect measure of interaction.

5. Conclusion

Various mixing rules of refractive index were used to test their legitimacy for binary liquid mixtures by using the measured values of density and refractive index. From the above investigation, it can be concluded that the above mentioned theoretical mixing rules perform well within the limits of experimental error.

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Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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